Prediction of Giant Electro-actuation for Carbon Nanoscrolls

R. Rurali,[1,2] V. R. Coluci,[3] and D. S. Galvão[3]

[1]*Laboratoire Collisions, Agrégats, Réactivité,*

IRSAMC, Université Paul Sabatier,

118 route de Narbonne, 31062 Toulouse cedex, France

[2]*Departament d'Enginyeria Electrònica,*

Universitat Autònoma de Barcelona 08193 Bellaterra, Spain

[3]*Instituto de Física "Gleb Wataghin",*

Universidade Estadual de Campinas,

C.P. 6165, 13083-970 Campinas SP, Brazil

(Dated: February 6, 2008)

Abstract

We study by first-principles calculations the electro-mechanical response of carbon nanoscrolls. We show that although they present a very similar behavior to carbon nanotubes for what concerns the axial deformation sensitivity, they exhibit a radial response upon charge injection which is up to one order of magnitude larger. In association with their high stability, this behavior make them a natural choice for a new class of very efficient nano-actuators.

With the advent of nanotechnology a great effort has been devoted to the study of nanostructures, carbon nanotubes (CNTs) [1] being one of the most studied. In spite of more than two decades of intense research, the detailed mechanism of tube formation remains unclear [2]. It has been proposed that CNTs could be a subsequent state of papyrus-like carbon structures, generally named carbon nanoscrolls (CNSs) [3, 4, 5, 6, 7, 8, 9](Fig. 1).

CNSs are remarkable structures sharing some of the rich mechanical and electronic properties exhibited by CNTs and potentially presenting new ones. They are known since the sixties from the pioneering work of Bacon [3] who first reported the growth of scroll whiskers. Surprisingly, very few studies [3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16] have been carried out for these systems. This can be explained in part by the intrinsic experimental difficulties in synthesis, purification, isolation, and characterization. However, after the recent advances in the low-temperature synthesis of CNSs [6, 7, 8] there is a renewed interested in these materials. Like CNTs, CNSs can be made of a single graphene sheet or by many of them. However, in contrast to CNTs, the scroll diameter can vary easily (expand or contract), thus they are extremely radially flexible. This property can be explored for a variety of technological applications, such as chemical doping, hydrogen storage, electro-actuation (mechanical deformation upon charge injection), etc..

The electro-mechanical response of CNTs has been investigated by means of first-principles calculations by Verissimo-Alves et $al.$ [17] and using an electron-lattice model by Gartstein et $al.$ [18]. The electron actuation effects are predicted to occur, but of limited magnitude - 0.2-0.3% - since the deformation of sp^2 carbon bond-lengths in close tubular structures as CNTs will require a significant amount of energy. An experimental demonstration of CNT based actuator has been reported by Baughman et $al.$ [19]. CNSs, on the other hand, are open structures and the radial expansion to accommodate the injected charges should be energetically more favorable. In this case it has simply to overcome the van der Waals interlayer interactions, instead of deforming sp^2 carbon bond-lengths, thus producing a more significant electro-actuation behavior. Recently, Braga et al. [15] have used classical molecular dynamics simulations to predict that CNSs should exhibit a significant radial expansion upon charge injection. However, it is not possible to have a reliable quantitative estimation using classical methods because quantum effects are not included, as well as it is not possible to differentiate between electrons and hole injections, which is known to produce a different response for CNTs [17, 18]. In order to properly address these issues the use

2

of full quantum methods is necessary. In this work we report such study for some selected scroll models.

We have carried out density-functional theory (DFT) calculations in the framework of the local density approximation (LDA) with the SIESTA code [20]. We have used a double-ζ basis set plus polarization functions and norm-conserving pseudopotentials of the Troullier-Martins type [21]. We have considered two prototype structures in supercell geometry (see Fig. 2): a zig-zag and an armchair-like CNS [15]. The Brillouin zone has been sampled with a converged grid of up to $1 \times 1 \times 12$ k-points. We have relaxed both the cell lattice vectors and the atomic positions, thus accounting for both the axial and radial response upon charge injection. We have also carried out a set of calculations where the lattice parameter was kept frozen, in order to explore complementary experimental situations, free standing actuator (like in Ref. 19) vs. sensor constrained between two electrodes.

In agreement with the molecular dynamics results of Ref. 15, we have chosen starting geometries with an internal radius of ~ 20Å. Larger systems, with a higher number of revolutions around the scroll axis - $i.e.$ obtained wrapping a wider graphite sheet - cannot be efficiently handled within DFT. However, the fundamental mechanisms and driving forces associated with the geometrical expansion/contraction upon charge injection are already qualitatively captured by the systems studied. Nonetheless, we have chosen CNS geometries which already present the critical overlap between sheet layers that assures the scroll formation [15]. We have injected a net charge of up to $\pm$ 0.055 | e | / atom into the systems by adding/removing electrons. In order to accommodate these extra/missing charges the carbon-carbon bond-lengths need to adjust their values and this is the origin of the electron-actuation phenomena.

The electro-actuation response relies on the competition between two different effects: an *electronic* actuation, driven by the depletion/population of bonding/anti-bonding states, and a purely *electrostatic* actuation, which originates from Coulomb repulsion. In the low-injection regime a contraction is expected upon electron removal (hole injection) due to the lack of bond completion, $i.e.$ creation of dangling bonds, which makes the region locally more reactive. Injecting electrons, on the other hand, results in a more complex situation. Adding electrons in anti-bonding states generates an electronic repulsion and some bond-lengths will elongate, but this, in turn, could stretch some of the neighboring bonds. In general, for sp^2 carbon based structures the best compromise is alternating short and long

bonds, even at the cost of breaking higher symmetries. This behavior is well-known for conducting polymers; for instance, in polymers containing benzenoid rings charge injection transform them into quinoid structures (with a well pronounced alternate of short and long bonds) [22]. Besides that, the picture is further complicated by the interplay with Coulomb forces induced by the extra charge injected that will tend to expand the scroll by pushing apart the overlapped layers. Full quantum calculations are then necessary to quantify these effects.

In Fig. 3 we present the results for the relative axial variation of the lattice parameter ($\delta l/l_0$). The dependence on the injected charges follows the general trends exhibit by (5,5) and (12,0) CNTs reported in Ref. 17. CNSs expand to accommodate the extra electrons and slightly contract when holes are injected. In the high-injection regime the Coulombian repulsion dominates and the CNSs expand regardless of the sign of the injected charge. Most importantly, the magnitude of response is very similar to the case of CNTs and can reach values of about 0.2 - 0.3 %.

On the other hand, for what concerns the radial response (which is shown in Fig. 4), the behavior of CNSs is completely different from CNTs. While for CNTs the actuation response is almost equally distributed between the axial and radial parts, we have found the latter to be up to one order of magnitude more intense for CNSs [23], being approximately 2.5 % for the highest injected charge considered. As can be seen, for small values of charge injection armchair and zig-zag CNSs behave differently, one contracts while the other expands, thus the different topologies are still playing an important role. For higher charge values - where the interlayer Coulomb interactions are expected to dominate - both structures converge to almost the same values, recovering an almost linear behavior; again a close parallel with the behavior of doping conducting polymer is observed [24].

The data reported in Fig. 4 correspond to calculations where the lattice parameter was constrained to its equilibrium value in the neutral state. This arrangement is intended to mimic the situation where the CNS has its extremities clamped, *i.e.* a suspended scroll. On the other hand, relaxing the lattice better approaches the situation where the CNS is on a surface and can freely move in the axial direction too. In this case, however, the dependence of the diameter on the injected charge turned out to much more irregular, especially in high-charge regime, and it is often accompained by an *elliptization* of the structure. The radial response is sometimes even larger, but difficult to reliably associate with the injected

4

charge. In other words, free-standing CNS on a surface behave axially as CNTs and have an enhanced, but noisy radial sensitivity; suspended CNSs, axially constrained, exhibit a giant and ordered radial electro-mechanical response.

Recent DFT calculations of neutral scroll have attributed a metallic character to armchair CNSs [16, 25]. Our DFT calculations are in very good agreement with the results of Pan *et al.* [16], as shown in Fig. 5. However, the scroll geometry that we have used differs significantly from theirs (as we had to perform several full relaxations - lattice and atomic positions - we had to use smaller structures). Hence, this is a hint that, at least at this scale, the electronic structure is at a first approximation insensitive to the size of the scroll. Zig-zag CNSs are predicted to have a small band-gap [25]. For both topologies, we have found that the electronic structure of CNSs around the Fermi level is determined by the border states (in agreement with the results reported by Pan *et al.* [16] for what concerns armchair CNSs), in analogy with carbon nanoribbons from which they are derived by wrapping [16, 26, 27].

In order to gain a further insight on the electro-actuation process we have studied the localization of the extra charge in the high-injection regime. In Fig. 6 we have plotted the difference between the electronic density of a zig-zag CNS with 0.055 extra electrons per atom and the electronic density of the same CNS in the neutral state, *i.e.* the extra electrons of the charged system. It can be seen that the excess charge accumulates in central region of the CNS and, with a clear discontinuity, close to the borders. On the other hand, analyzing the relative elongation of each individual bond we have found that almost all the bonds elongate in a similar way, despite the excess charge is not homogeneously distributed. The charge accumulated at the CNS boundary carries the large radial electro-mechanical response, due to efficient inter-layer Coulombian repulsion; the excess charge concentrated in the central region, on the other hand will only be responsible of minor bond elongations, contributing to both axial and radial response. However, in the high-injection regime, the bond deformation is uniformly distributed along the CNS. This is no longer true for low-injected charge, where the predicted alternation of shortened and elongated bonds is recovered.

Therefore, the electro-mechanical actuation in the high-charge regime also originates in the charge accumulation in the central region of the CNS. In the studied geometry, presenting a limited layer overlap, this charge has only a minor impact in local bond elongation. In CNSs with a larger layer overlap also the extra charge concentrated in the CNS center could contribute with an efficient inter-layer Coulomb repulsion. Hence we do not discard

that, in absence of other side effects, *e.g.* inter-layer sliding, could not lead to a larger electro-mechanical response.

In summary, we have carried out *ab initio* DFT calculations of the electro-actuation effect in carbon nanoscrolls. While the axial sensitivity of CNSs has very similar features than in carbon nanotubes, the radial response has a completely distinct behavior, reaching under high-charge injection conditions the giant relative diameter variation of 2.0-2.5 %, which is one order of magnitude higher than the values reported for CNTs. In suspended CNS is much easier to correlate the charge injection with the electro-mechanical response, as the circular symmetry of the scroll is qualitatively maintained for a wide range of injected charge. Free-standing CNS are more naturally used as axial actuators, even though in such a case their response is similar to the case of CNTs. These results suggest that CNSs provide a simple and flexible path towards the development of efficient electro-mechanical actuators at the nanoscale. We hope the present study to stimulate further experimental work to test these predictions.

---

[1] S. Ijima, Nature (London) **354**, 56 (1991).

[2] W. A. de Heer, P. Poncharal, C. Berger, J. Gezo, Z. M. Song, J. Bettini, and D. Ugarte, Science **307**, 907 (2005).

[3] R. Bacon, J. Appl. Phys. **31**, 283 (1960).

[4] O. Zhou, R. M. Flemming, D. W. Murphy, C. H. Chen, R. C. Haddon, A. P. Ramirez, and S. H. Clanum, Science **263**, 1744 (1994).

[5] W. Ruland, A. K. Schapper, H. Hou, and A. Greiner, Carbon **41**, 423 (2003).

[6] H. Shioyama and T. Akita, Carbon **41**, 179 (2003).

[7] L. M. Viculis, J. J. Mack, and R. B. Kaner, Science **299**, 1361 (2003).

[8] Z. Khang, E. Wang, L. Gao, S. Lian, M. Jiang, C. Hu, and L. Xu J. Am. Chem. Soc. **125**, 13652 (2003).

[9] J. C. Lauin, S. Subnamoney, R. S. Ruoff, S. Berber, and D. Tománek, Carbon **40**, 1123 (2002).

[10] A. Ameclinckx, D. Bennates, X. B. Zhang, G. van Thendeloo, and J. van Landuyt, Science **267**, 1334 (1995).

[11] V. Z. Mordkovich, M. Baxendale, S. Yoshimura, R. P. H. Chang, Carbon **34**, 1301 (1996).

[12] Y. Maniwa, R. Fujiwara1, H. Kira1, H. Tou1, E. Nishibori, M. Takata, M. Sakata, A. Fujiwara, X. Zhao, S. Iijima, and Y. Ando, Phys. Rev. B **64**, 073105 (2001).

[13] D. Tománek, W. Zhong, and E. Krastev, Phys. Rev. B **48**, 15461 (1993).

[14] D. Tománek, Physica B **323**, 86 (2002).

[15] S. F. Braga, V. R. Coluci, S. B. Legoas, R. Giro, D. S. Galvão, and R. H. Baughman, Nano Lett. **4**, 881 (2004).

[16] H. Pan, Y. Feng, and J. Lin, Phys. Rev. B **72**, 085415 (2005).

[17] M. Verissimo-Alves, B. Koiller, H. Chacham, and R. B. Capaz, Phys. Rev. B **67**, 161401(R) (2003).

[18] Y. N. Gartstein, A. A. Zakhidov, and R. H. Baughman, Phys. Rev. Lett. **89**, 045503 (2002).

[19] R. H. Baughman, C. X. Cui, A. A. Zakhidov, Z. Iqbal, J. N. Barisci, G. M. Spinks, G. G. Wallace, A. Mazzoldi, D. De Rossi, A. G. Rinzler, O. Jaschinski, S. Roth, and M. Kertesz, Science **284**, 1340 (1999).

[20] P. Ordejón, E. Artacho and J. M. Soler, Phys. Rev. B **53**, R10441, (1996); J. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón and D. Sánchez-Portal, J. Phys.: Condens. Matter, **14**, 2745 (2002); see also http://www.uam.es/siesta/

[21] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[22] D. S. Galvão, D. A. dos Santos, B. Laks, C. P. de Melo, M. J. Caldas, Phys. Rev. Lett. **63**, 786 (1989).

[23] A detailed comparison with equivalent results for CNTs is not possible. In Ref. 18 the authors restrict to very small charge injection ($| e | $/atom $= 0.005$). Ref. 17 investigates a wider range of electron/hole injection, comparable to ours, but they only report the results concerning the axial response, suggesting, however, that the radial behavior is qualitatively similar.

[24] *Handbook of Conducting Polymers*, edited by T. A. Skotheim (Dekker, New York, 1986).

[25] No data other than ours on the *ab initio* electronic structure of zig-zag CNSs are available at present. We are currently performing an extensive study of a wide range of scroll geometries to generalize our conclusions.

[26] M. Fujita, K. Wakabayashi, K. Nakada, and K. Kusakabe, J. Phys. Soc. Jpn. **65**, 1920 (1996).

[27] K. Nakada, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. B **54**, 17954 (1996).

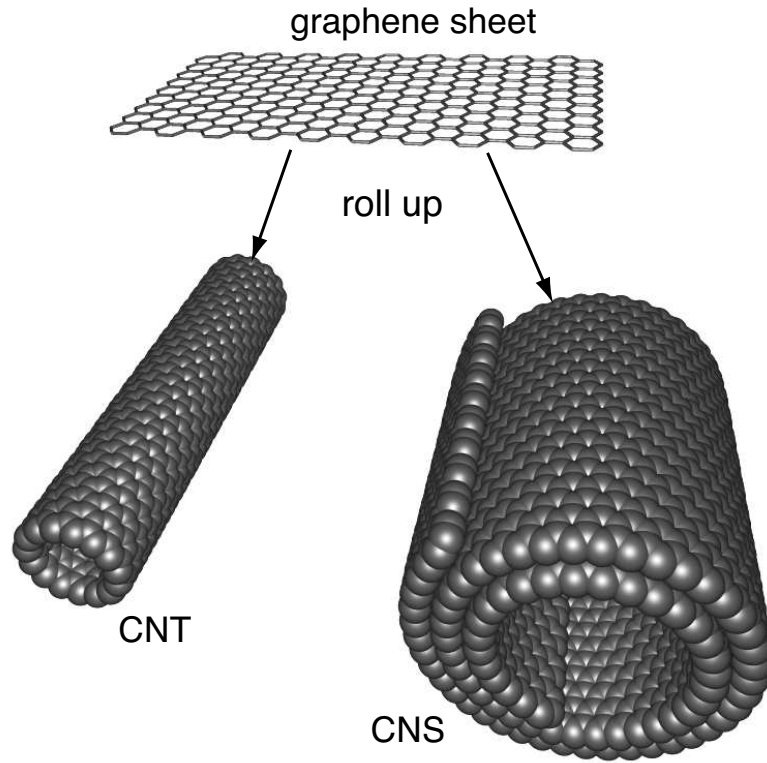graphene sheet

roll up

CNT

CNS

FIG. 1: Carbon nanotubes and scrolls can be topologically considered as cylindrical and papyrus-like structures, respectively, obtained from rolled up graphene layers.
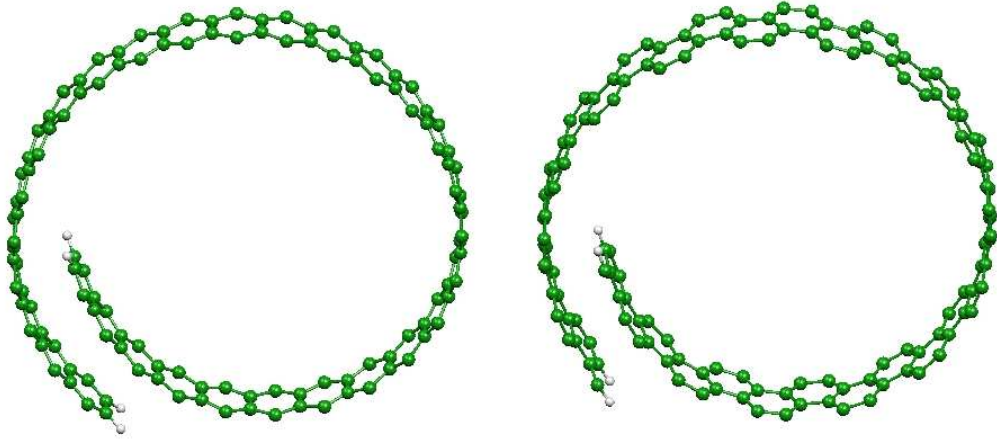
FIG. 2: (color online) Unit cells used in the calculations of (a) an armchair and (b) a zig-zag CNS. We have followed the nomenclature introduced by Braga *et al.* [15], in turn derived from previous works on carbon nanoribbons [26, 27].
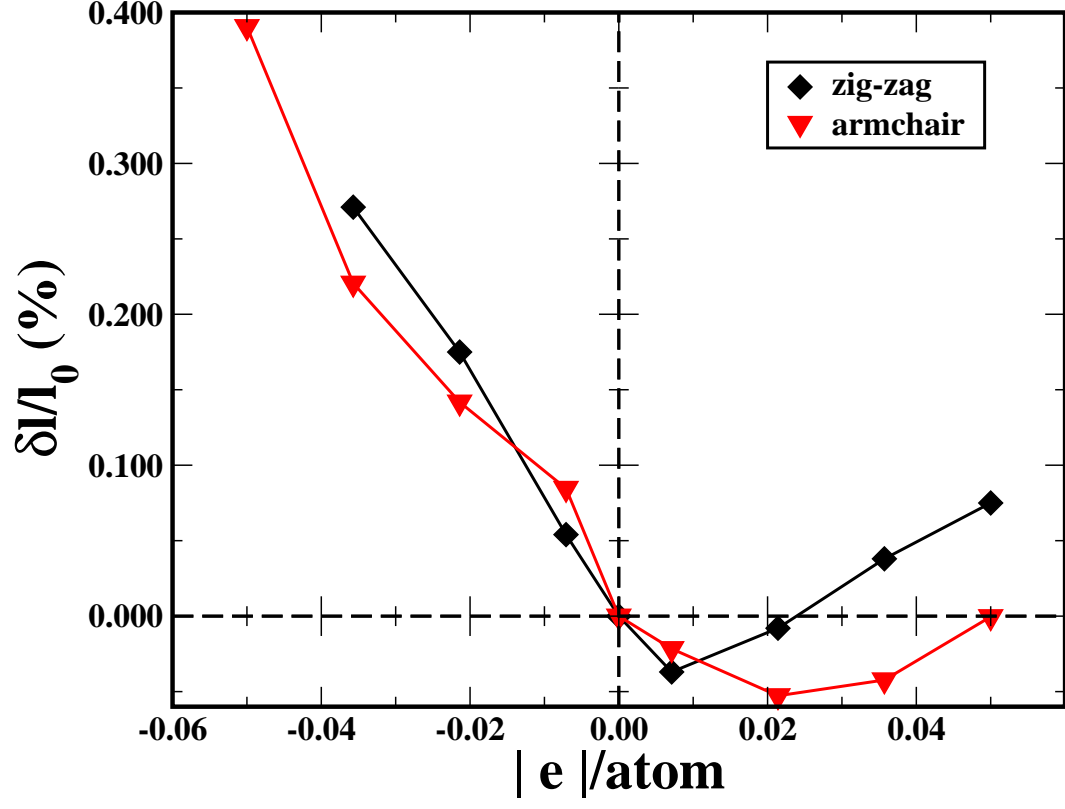
FIG. 3: (Color online) Relative variation of the unit cell lattice parameter l upon charge injection with respect to its equilibrium value in the neutral state l_0.
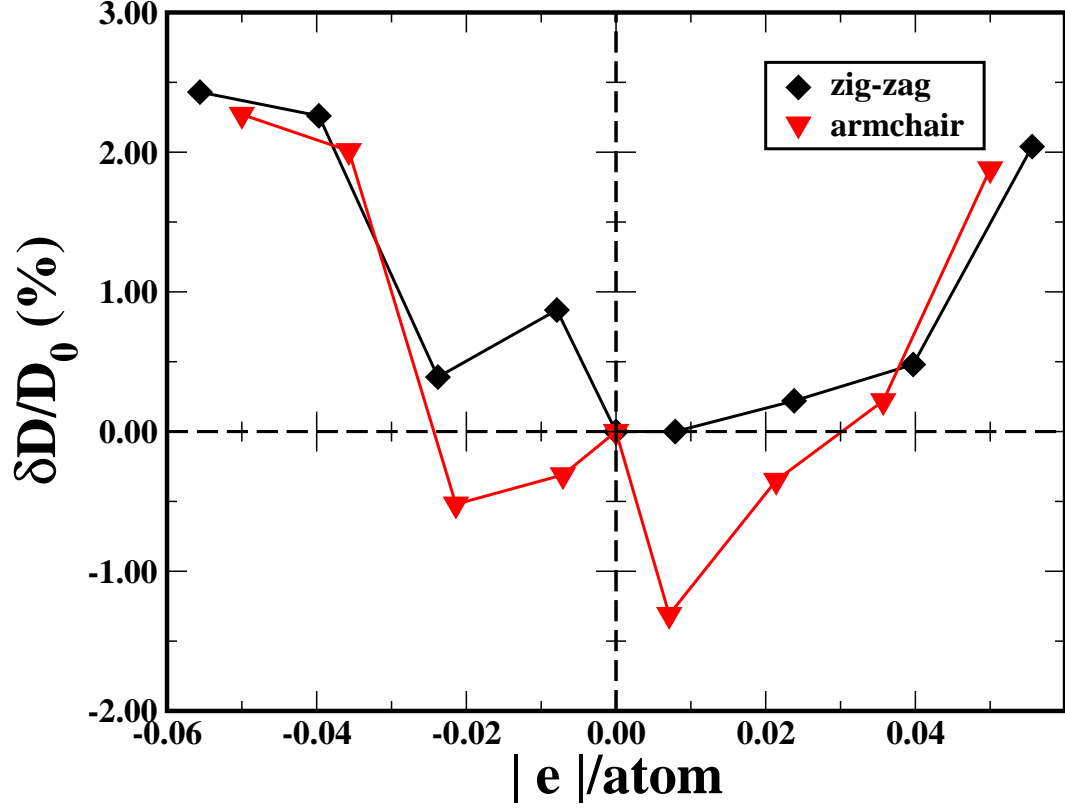
FIG. 4: (Color online) Relative variation of the CNS diameter parameter D upon charge injection with respect to its equilibrium value in the neutral state D_0. The diameter D has been defined as the maximum distance between two carbon atoms with same axial coordinate.
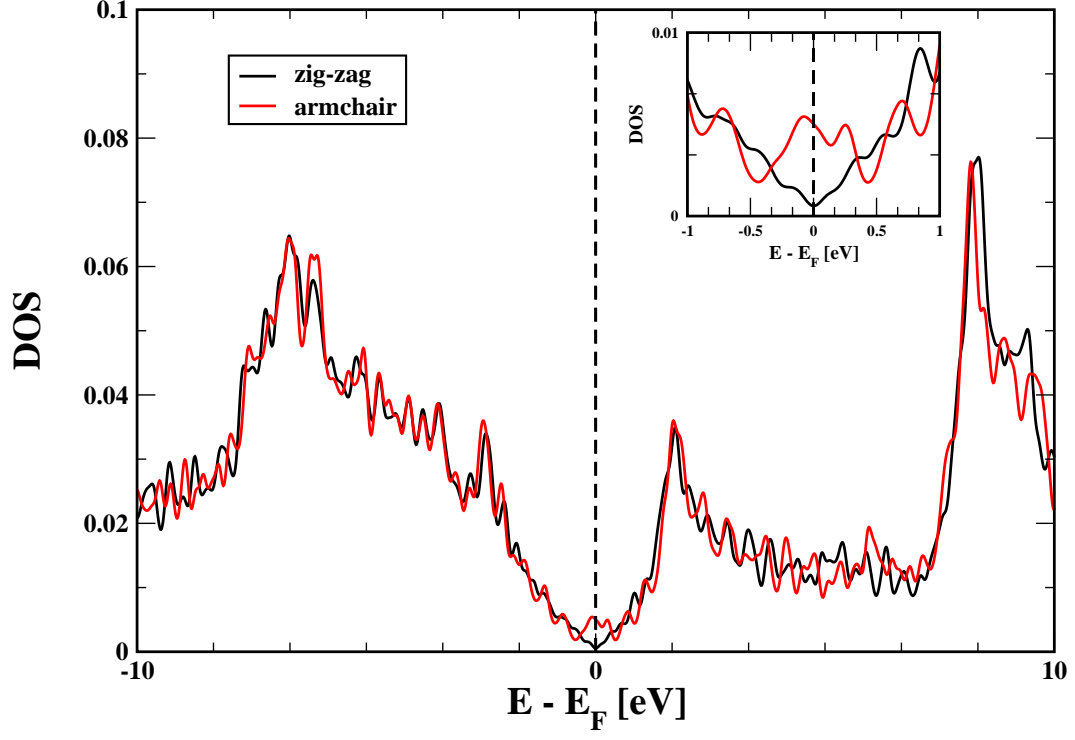
FIG. 5: (Color online) Electronic density of states of the armchair (red line)and the zig-zag (black line) CNS studied. The inset panel shows a magnified view around the Fermi level.
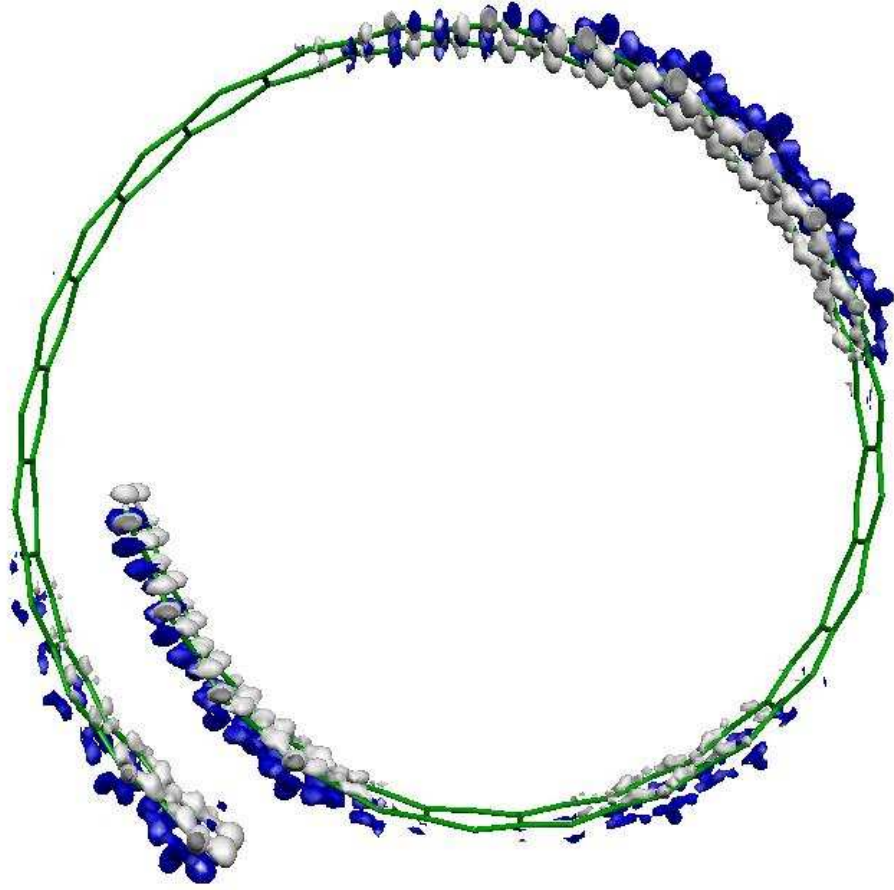
FIG. 6: (Color online) Distribution of the extra charge of -0.055 $| e |$ /atom in a zig-zag CNS.